

SUMMARY REPORT
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A REVIEW OF THE STABILITY OF METALLIZED
POLYMERS AND DIELECTRICS EXPOSED
TO THE DEGRADING INFLUENCES OF SPACE ENVIRONMENT

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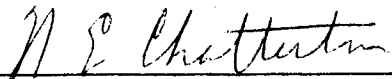
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ABSTRACT

The stability of metallized polymers and dielectrics exposed to the space environment is reviewed. The data on the degradation of those mirrors are a summary of the present knowledge. A survey is also made about the problems of attaching an OSR to substrate and to spacecraft skin. Main emphasis is given to silvered and aluminized Teflon mirrors. The effects of temperature and radiation encountered in space on the mechanical and chemical properties of polymers, especially TFE and FEP Teflons, are discussed since the polymer "sees" space and the Sun.

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INTRODUCTION

One of the many important facets of the complex problem of spaceflight is that of environmental control of the space vehicle. The control of spacecraft temperature is usually accomplished by passive methods, generally by the selection of appropriate surfaces and coatings to provide optimum reflectance, absorptance, and emittance of solar and infrared radiation. The major problem encountered with the thermal control coatings now in use is the change in the solar-absorptance-to-thermal-emittance ratio (α_s/ϵ) of the coatings as a result of solar ultraviolet radiation and charged particle bombardment. This change causes an increase in the temperature of the interior of the spacecraft, degrading the performance of the equipment aboard.

With the launching of satellites and space stations intended to operate for a decade in the space environment, the development of space-stable thermal control coatings becomes more imperative. Over the last decade a great deal of work has been carried out in the field of spacecraft thermal control materials development. The initial efforts were directed mainly at establishing engineering tolerances and design parameters. Now, however, the state of the art demands that more detailed studies be performed in order to elucidate more definitely the damage mechanisms associated with the types of radiation encountered in space.

The materials required for the passive temperature control are materials with low α_s -to- ϵ ratio, i. e., materials that reject a major portion of the solar energy and effectively radiate thermal energy at low temperature. This requirement is met by white paints typified by metal-oxide "pigments" blended with organic, semiorganic,

or inorganic "binders". These white paints are easy to apply and are mechanically stable in the prelaunch, launch, and orbital environments. However, as flight evidence shows, most paints degrade in the space radiation environment and the solar absorptance (α_s) of these coatings increases. The degradation mechanisms that produce the instability are quite complex and must be understood sufficiently before attempting to develop new coatings having long-term stability for space station application.

In addition to paints, the requirement for low α_s -to- ϵ ratio can be achieved with a coating over a good solar reflector such as polished aluminum or silver. The coating must be transparent in the wavelength range of high solar intensity but "black" in the infrared range of low temperature thermal radiation. The same effect can be achieved by metallizing one side of a transparent material placed so the transparent material "sees" the Sun and space.

Optical Solar Reflectors (OSR) having vacuum-deposited silver on thin sheets of fused silica were developed based on the above principle. These were found to be stable in the space environment. These OSRs supply an alternate solution to thermal control at some cost and weight penalty. The problems associated with the bonding of these OSRs to the spacecraft skin and to curved surfaces are well-known. All these problems have made the use of OSRs very difficult for spacecraft thermal control.

The weight problem of OSR has been considerably reduced now by vacuum-depositing silver or aluminum on thin sheets of Teflon. This also solves the problem of attaching an OSR on a curved surface, since Teflon is not rigid like fused silica. Although the problems of weight and rigidity have been solved, the problem of attaching these metallized Teflons to the vehicle skin still remains, as it was with

metallized fused silica. If an adhesive system is used, then the outgassing in vacuum and the effect of radiation on the adhesive must be taken into account. The other problem which should be investigated is the effect of temperature and space radiation on Teflon since it "sees" the Sun and space. To date, very little has been done on the effect of radiation (such as ultraviolet, protons, and electrons) on Teflon, its stability under long-time exposure to radiation, etc. The use of metallized Teflon as a thermal control surface for Skylab and space station applications depends on the laboratory and flight tests conducted on the stability of Teflon and the Teflon mirrors.

This report deals with the present knowledge about the fused silica and Teflon mirrors, the effect of radiation on them, and the problems of attaching them to the vehicle skin. At the end is a discussion about the effects of temperature and radiation on the mechanical properties of polymers, especially TFE and FEP Teflons, to show what temperature and different types of radiation can do to the polymers.

RESULTS

RADIATION DEGRADATION

Optical Solar Reflectors (OSR)

OSR is a coating system which is based on the optics of a second-surface mirror and utilizes selective spectral absorptance. Over the wavelength range of the solar spectrum it is highly reflecting, and in the infrared region it has a high thermal emittance. In its most radiation-resistant form, the second-surface mirror consists of vacuum deposited silver on a fused-silica substrate (Corning fused silica #7940) with a thickness of about 0.008 inch. This combination yields $\alpha_s = 0.050$ and $\epsilon = 0.81$ at 295°K. The high reflectance of solar energy is a result of the second-surface Ag-film, whereas the high ϵ is produced by the fused silica, which is transparent throughout the solar wavelength region and primarily opaque in the infrared region beyond 4.5 microns. To provide protection to the back surface against corrosion and during handling, 500 to 1,000 angstroms of Inconel is deposited on the silver film. The spectral reflectance along with the total hemispherical emittance and α_s/ϵ ratio of the above mentioned OSR are shown in Figures 1 and 2 as measured by Lockheed Palo Alto Research Laboratory (Ref. 1).

Figure 3 shows the effects of ultraviolet radiation on the Si_2O_3 overcoated stretch-formed aluminum mirrors (Ref. 2). The samples were irradiated at various temperatures up to 80°C for exposures up to about 9,800 equivalent space Sun hours (ESSH). The mirrors exhibited a negligible dependence of damage (ΔR_s) on irradiation temperature.

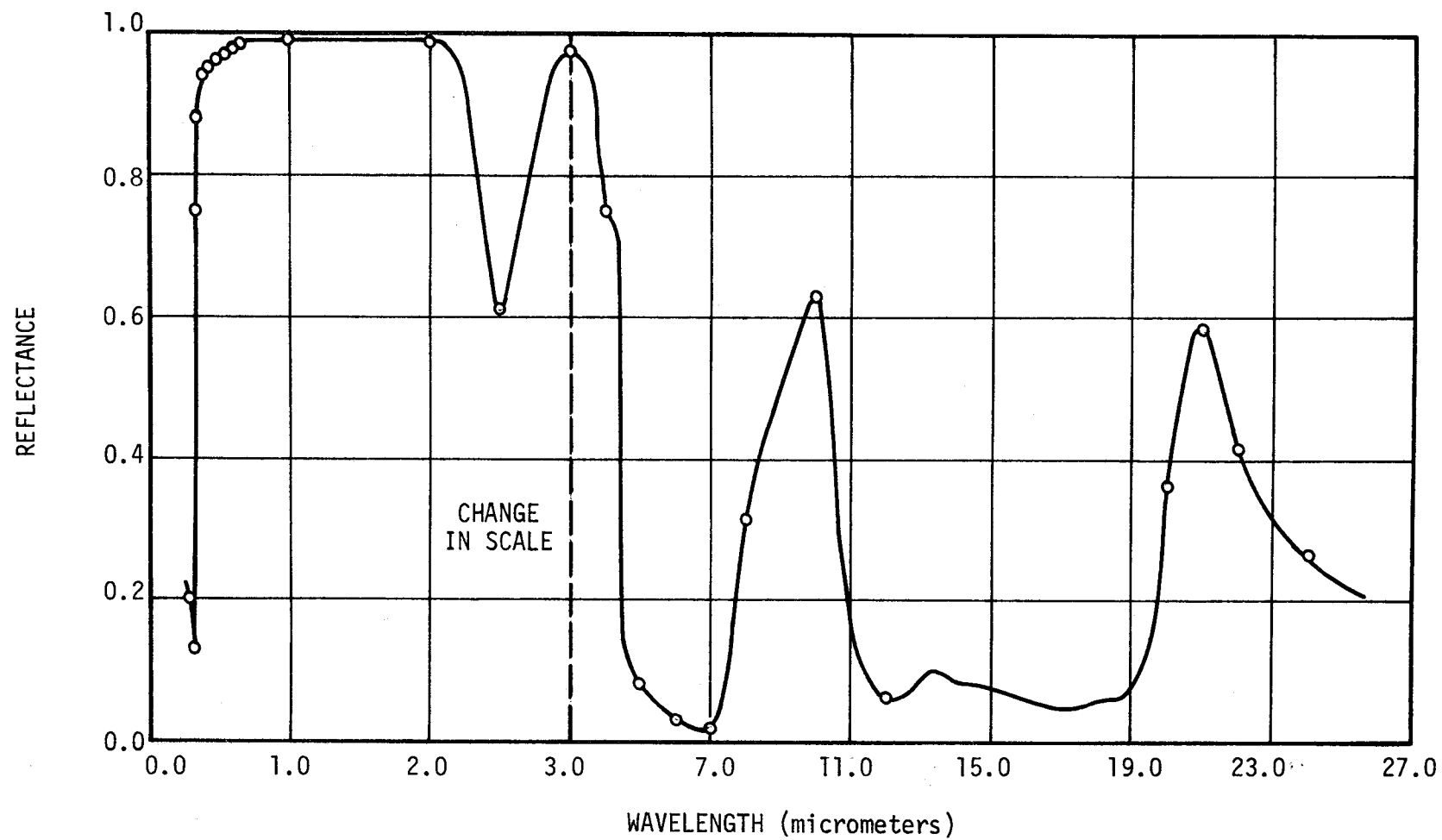


FIGURE 1. NEAR-NORMAL SPECTRAL REFLECTANCE OF OSR

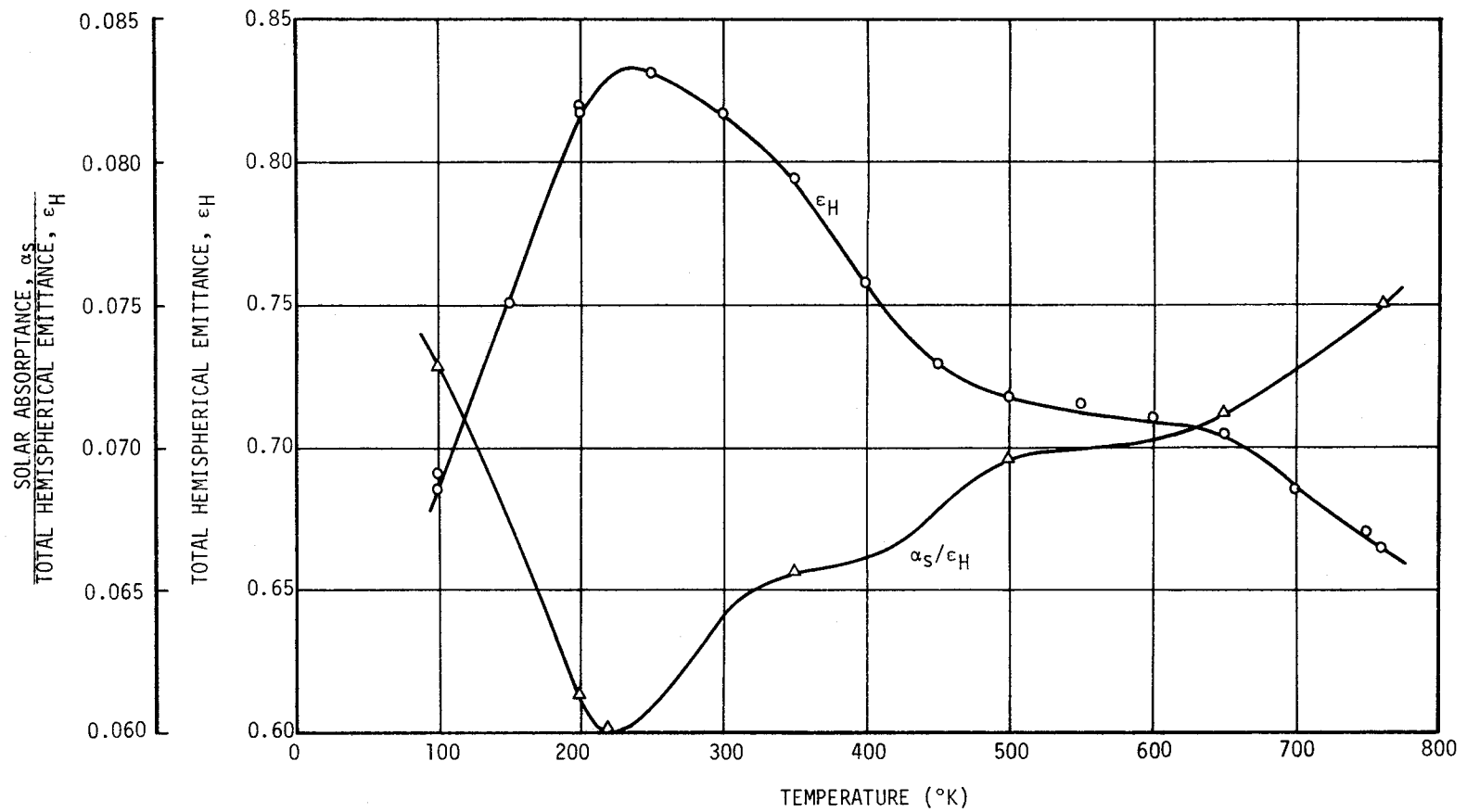


FIGURE 2. 0.008-INCH FUSED SILICA SECOND-SURFACE MIRROR

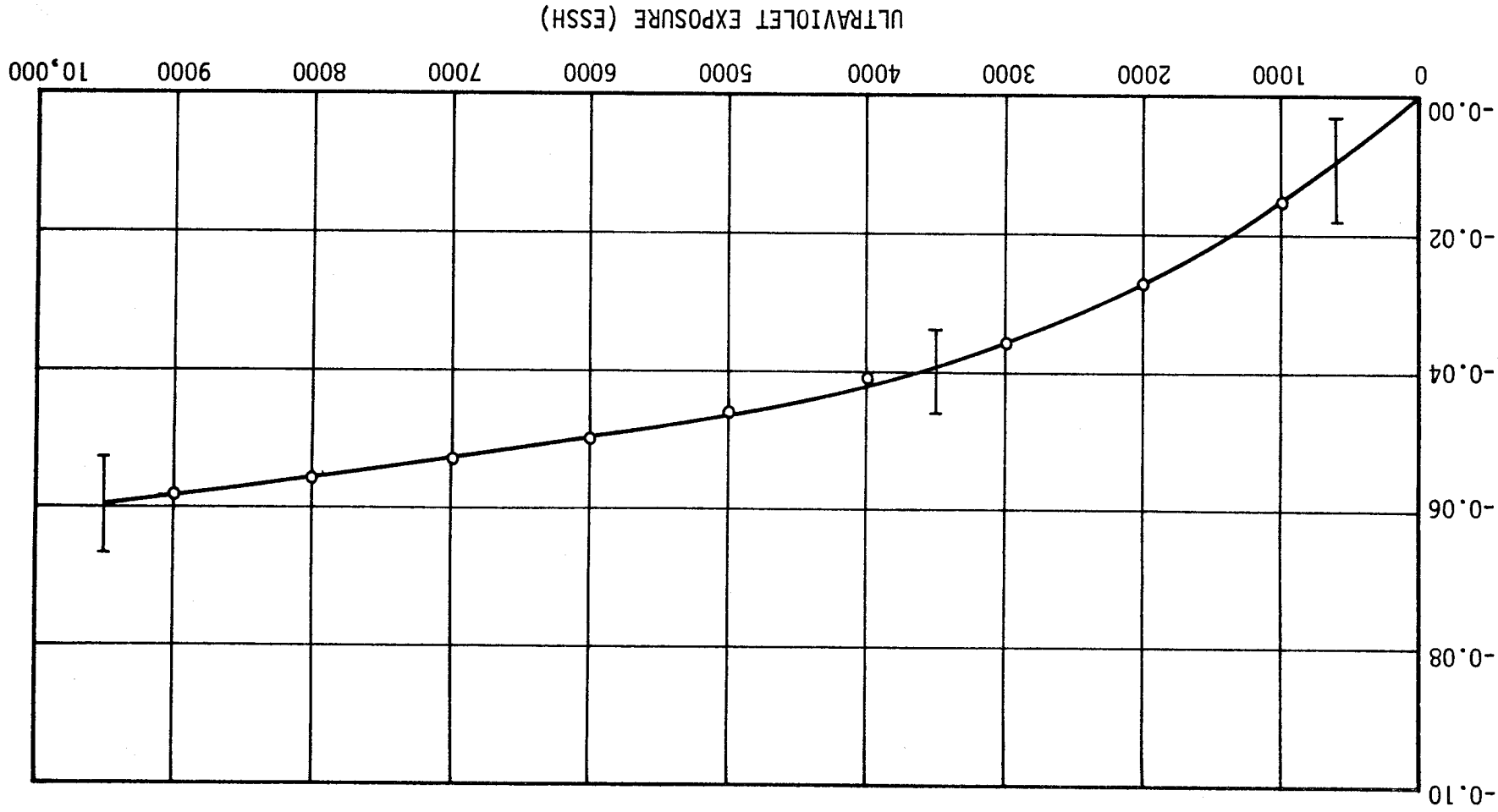
CHANGE IN SOLAR SPECULAR REFLECTANCE, ΔR_s 

FIGURE 3. EFFECT OF ULTRAVIOLET RADIATION ON THE SOLAR REFLECTANCE OF SiO_2 OVERCOATED STRETCH-FORMED ALUMINUM MIRRORS

To evaluate the effects of proton integrated flux, and mirror temperature on the optical damage, Boeing ran some tests at temperatures of -195° , 0° , and 50°C at integrated flux levels of 5×10^{16} , 1×10^{17} , and 2×10^{17} protons/cm². Results of the integrated flux/temperature experiment are shown in Figure 4. The vertical bars represent the spread in data between identical samples and are shown wherever a significant spread occurred. Reflectance measurements performed at various time increments after irradiation showed that the reflectance continued to decrease even up to 362 hours after irradiation. Thus, the points of the -195°C curve may even get higher when long-time measurements are made.

Metallized Polymer

Basically metallized polymers are also second-surface mirrors, where the requirement for low α_s -to- ϵ ratio is achieved with a transparent coating over a good solar reflector. The same effect is achieved by metallizing one side of a transparent material, placed so the transparent material "sees" the Sun and space. In general, aluminum or silver is vacuum-deposited over thin sheets of TFE Teflon or FEP Teflon. The silver or aluminum surface is protected from atmospheric contamination in the prelaunch period by its intimate contact with the Teflon. Protection is provided to the back surface of the silver or aluminum by an overcoating of vacuum-deposited inconel.

II TRI's results (Ref. 3) concerning the effect of ultraviolet radiation on the reflectance of an aluminized FEP Teflon mirror obtained from JPL are shown in Figure 5. Although this material was not included on Pegasus III, it was flown on Mariner V. No gas adsorbate studies were performed on these FEP Teflon mirrors. For comparison the effect of ultraviolet radiation on the reflectance of Z93 and zinc

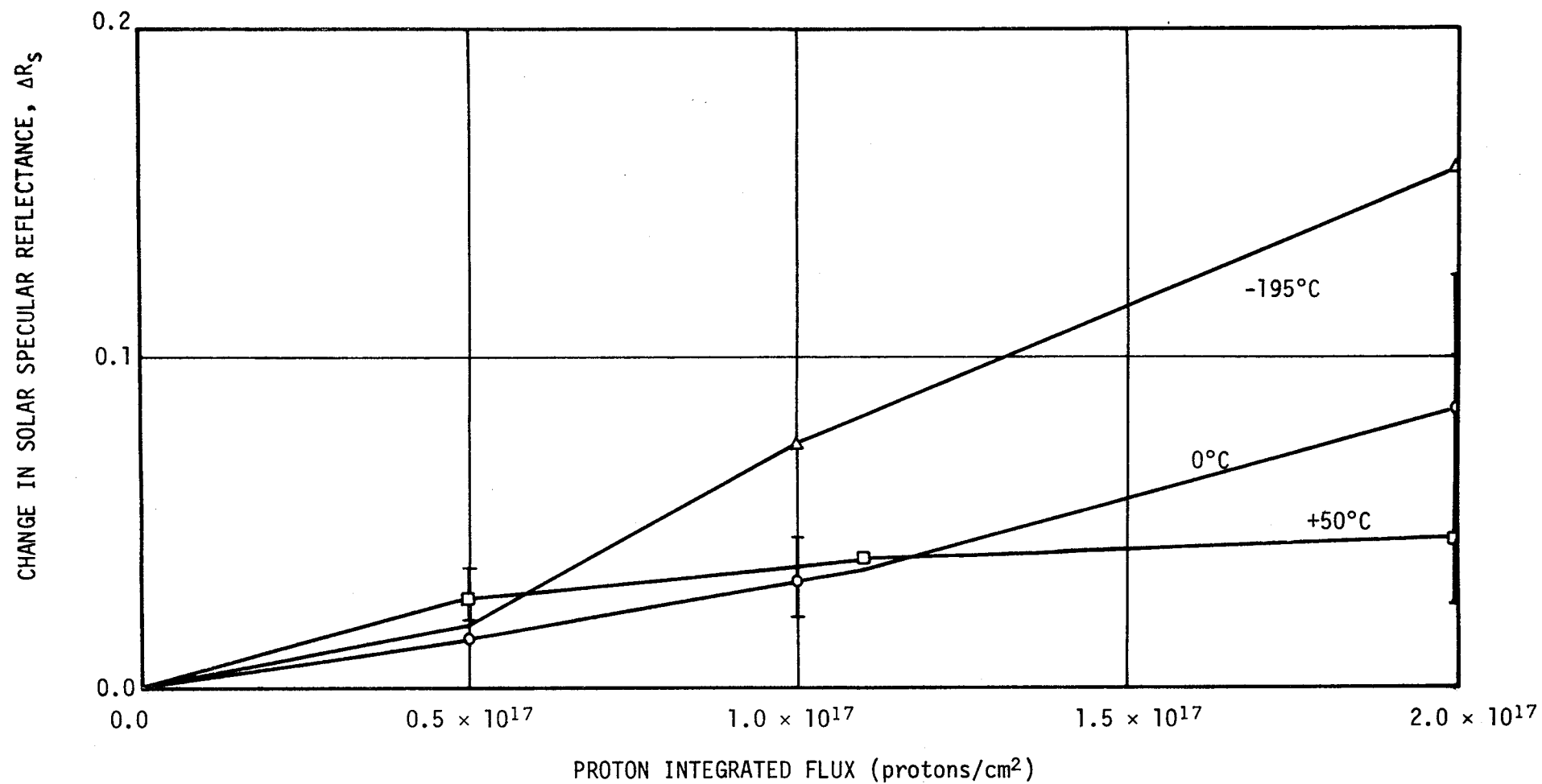


FIGURE 4. EFFECT OF PROTONS ON THE SOLAR SPECULAR REFLECTANCE OF Si_2O_3 OVERCOATED STRETCH-FORMED ALUMINUM MIRROR

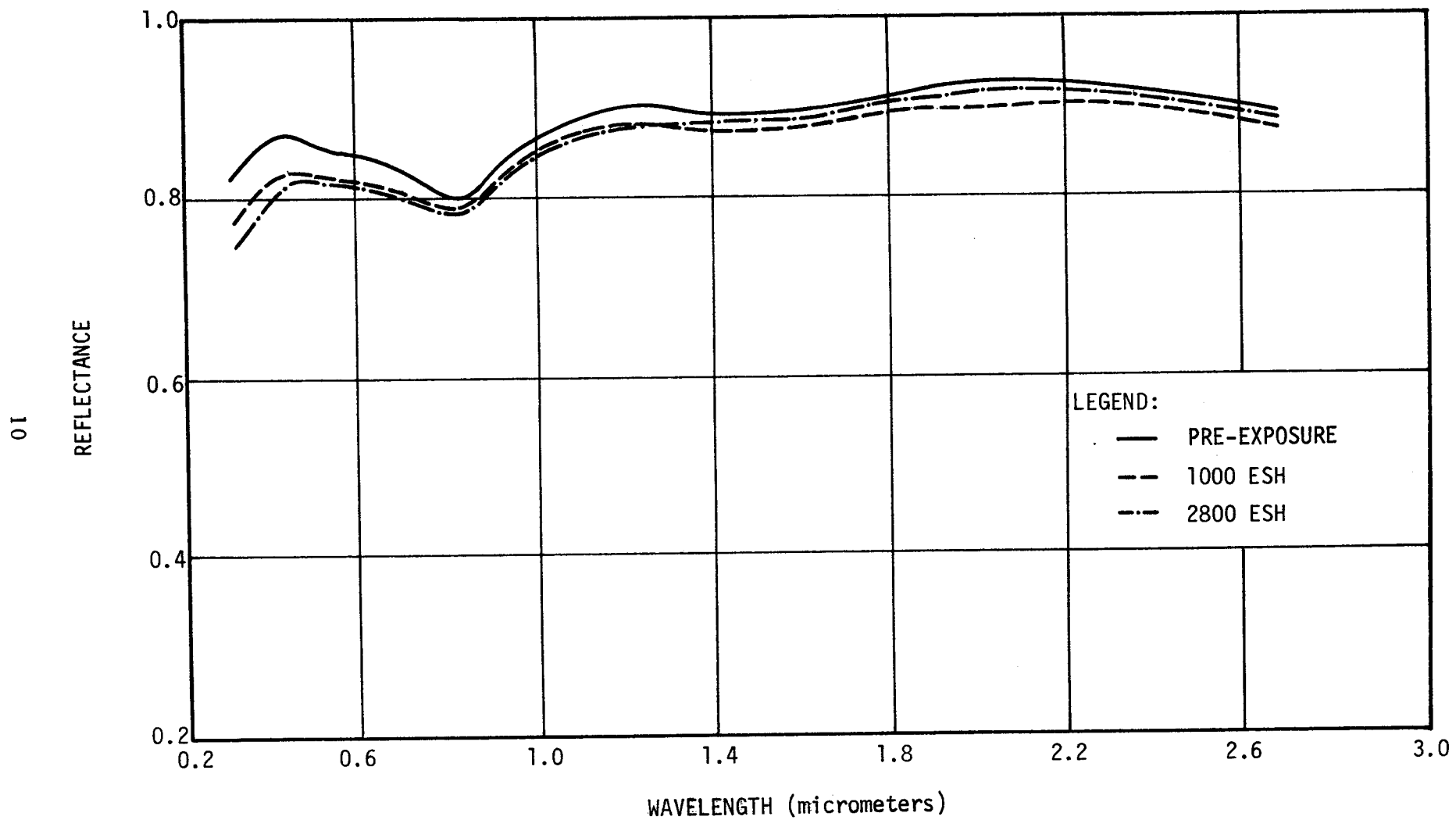


FIGURE 5. EFFECT OF ULTRAVIOLET RADIATION ON THE REFLECTANCE OF ALUMINIZED FEP TEFLON

orthotitanate is also shown in Figures 6a and 6b. From these curves it appears that at 0.50 micron the change in reflectance for aluminized Teflon is about 4 percent whereas that for Z93 and Zn_2TiO_4 is about 6 percent. The change in reflectance at lower wavelengths will be much higher for aluminized Teflon than it will be for Z93, as can be seen from these figures.

Figure 7 shows the effect of solar radiation on the reflectance of aluminized mylar obtained from Langley Research Center in two wavelength bands: 0.30 to 0.40 micrometer and 0.30 to 0.65 micrometer. This is flight data obtained from the ATS-3 satellite (Ref. 4).

The effect of electron irradiation on the reflectance of aluminized FEP type A Teflon and silvered FEP type A Teflon was studied by The Boeing Company (Ref. 5). These metallized Teflons are probably made by Goddard Space Flight Center, although no mention has been made by Boeing about the source of these Teflon mirrors. Their results for fluences of 10^{13} , 10^{15} , and 10^{16} electrons/cm² are reproduced in Figures 8 and 9.

The metallized FEP Teflon resists reflectance degradation from 80 keV electrons until fluences greater than 10^{15} electrons/cm² are reached. All the varieties studied are altered significantly by exposure to 10^{16} electrons/cm² at 80 keV. The Teflon loses its transparent nature, and therefore its specular quality, and acquires a crazed, mottled-gray appearance.

A recent study of the silvered FEP Teflon (Ref. 6) showed degradation at 5×10^{10} protons/sec/cm². The degradation was essentially in the region of 0.80 to 0.30 microns. These mirrors were then exposed to higher energy protons with the hope of getting more degradation and to find possible chain scission. Surprisingly, these

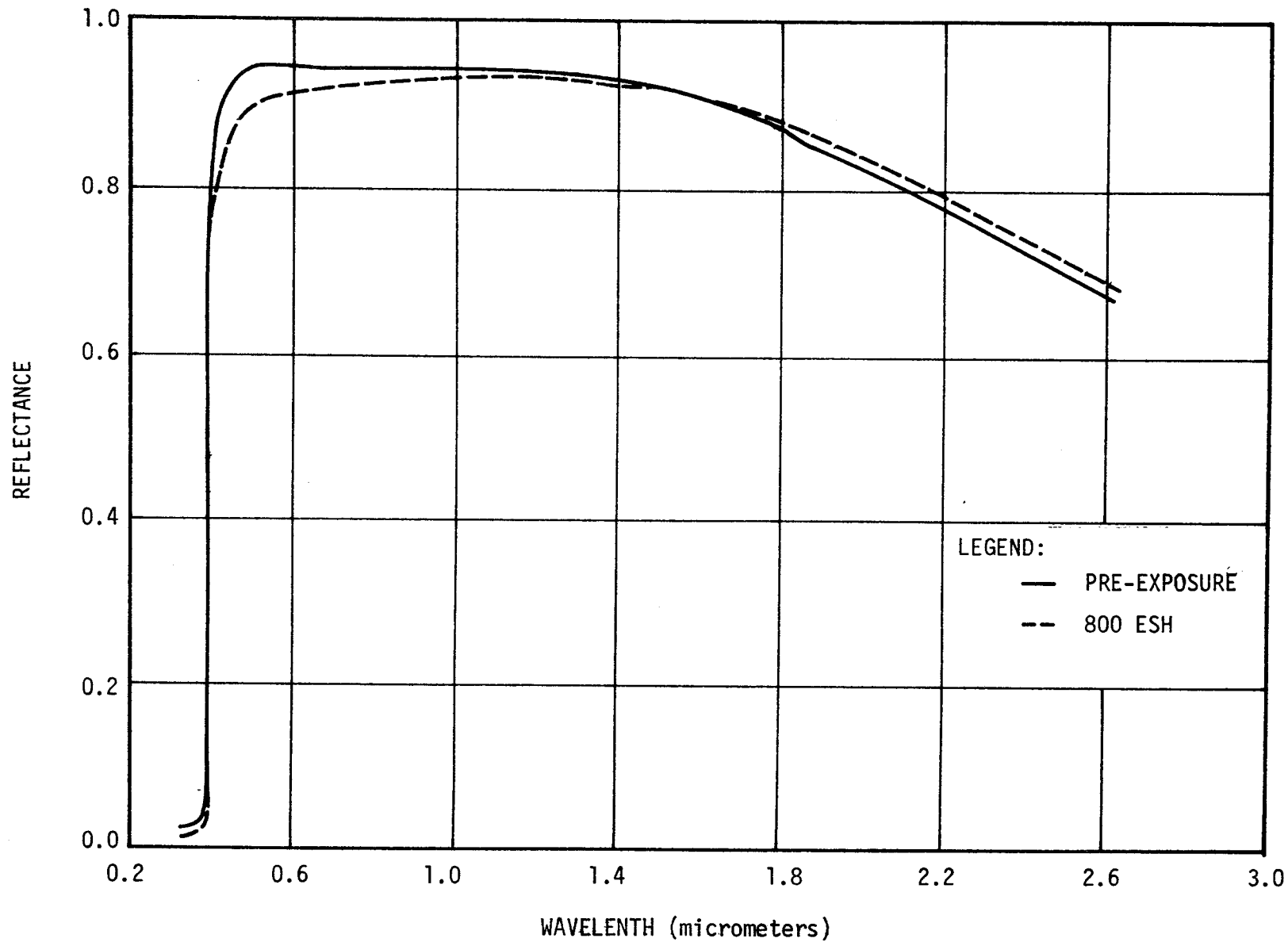


FIGURE 6a. EFFECT OF ULTRAVIOLET RADIATION ON THE REFLECTANCE OF Z93

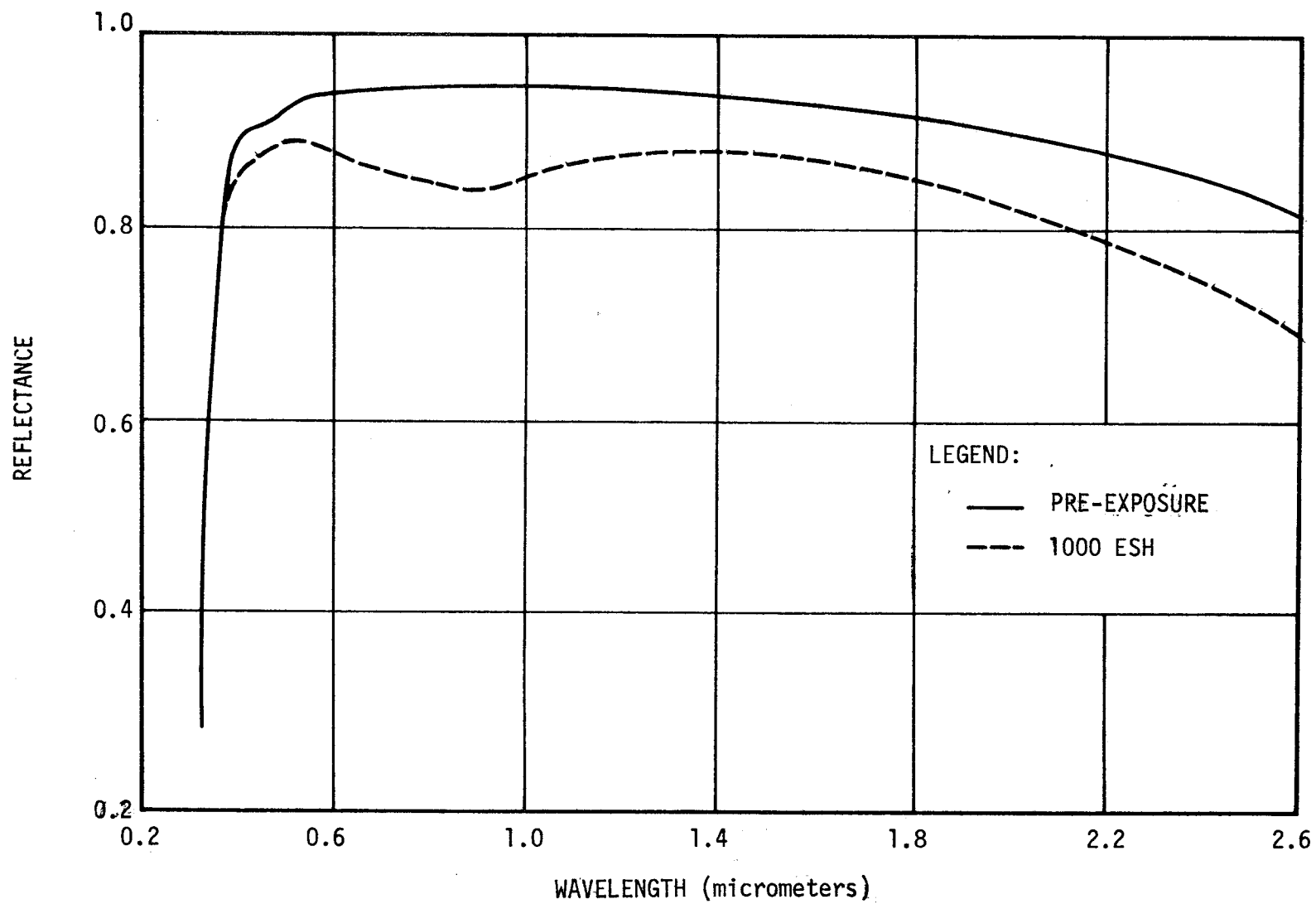


FIGURE 6b. EFFECT OF ULTRAVIOLET RADIATION ON THE REFLECTANCE OF PLASMA CALCINED ZINC ORTHOTITANATE

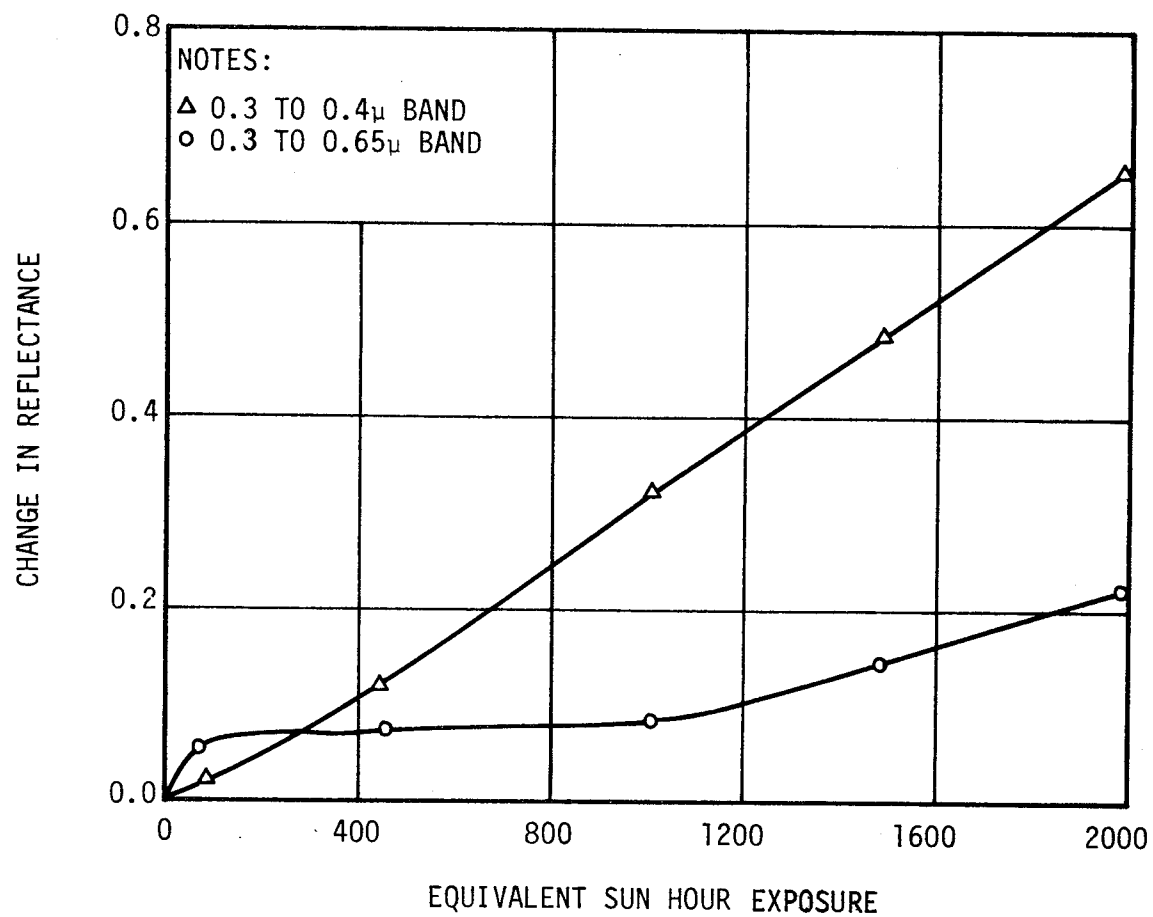


FIGURE 7. EFFECT OF SOLAR RADIATION ON THE REFLECTANCE OF ALUMINIZED MYLAR

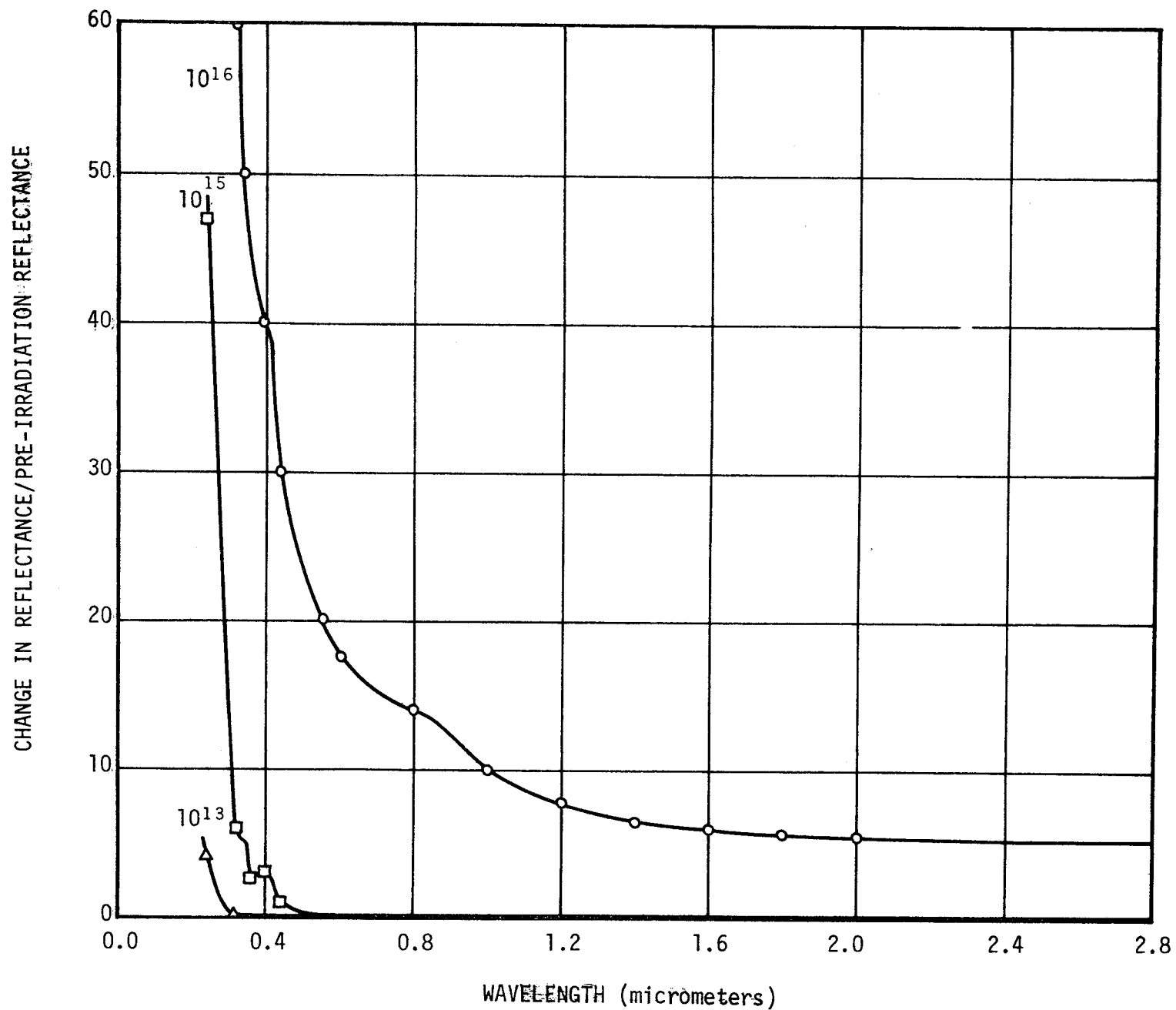


FIGURE 8. EFFECT OF 80-keV ELECTRONS ON THE REFLECTANCE OF ALUMINIZED 5-mil FEP TEFLON

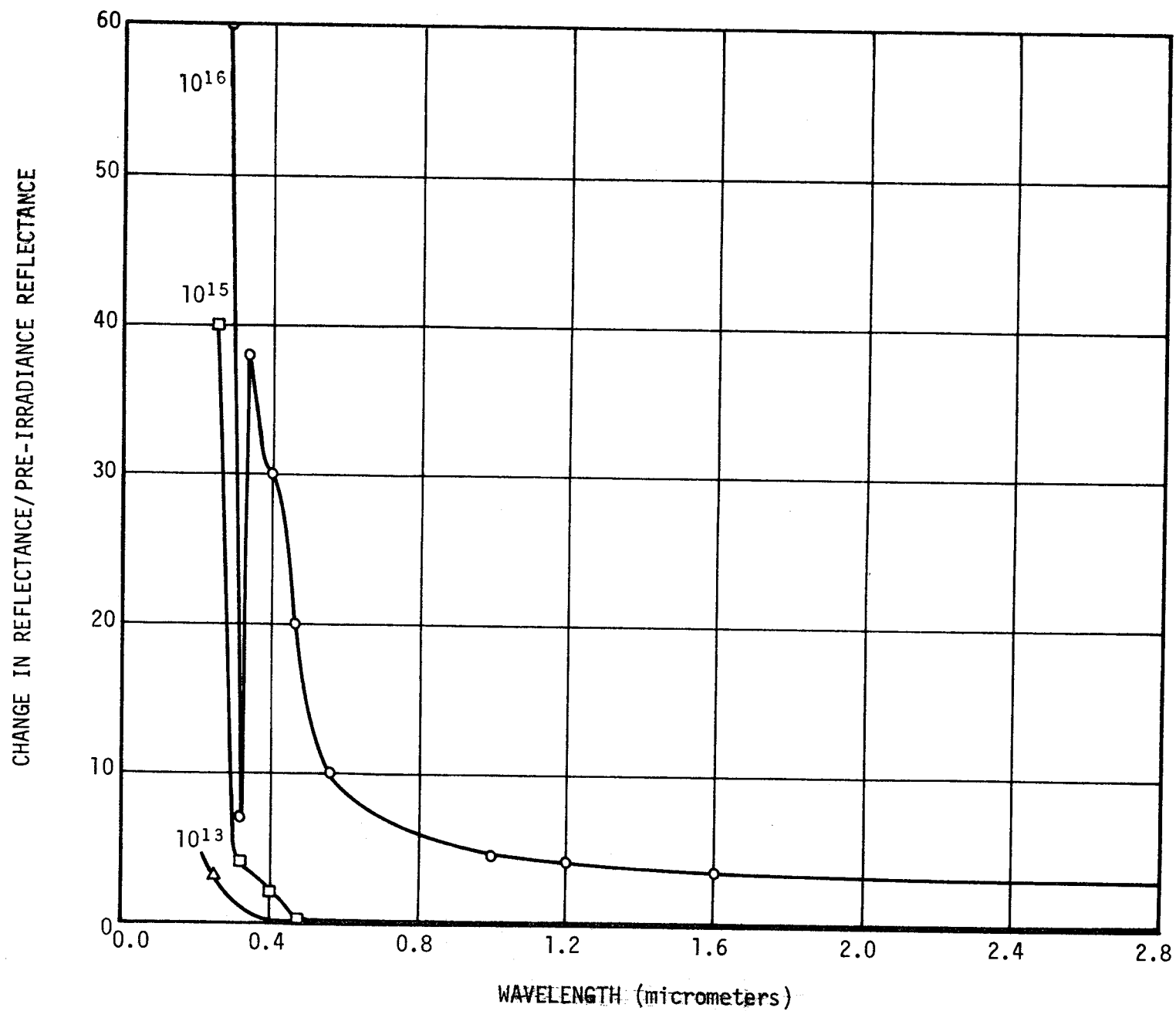


FIGURE 9. EFFECT OF 80-keV ELECTRONS ON THE REFLECTANCE OF SILVERED 2-mil FEP TEFLON

mirrors showed no degradation in their reflectance behavior. It is felt that high energy protons pass through the polymer without an interaction with it. The study of degradation of the silvered FEP Teflon with low-energy protons is in process. The effect of low-energy protons (1×10^{15} protons/cm²-hr at 3 keV) on the transmission of FEP Teflon has been studied by General Electric (private communication). The transmission in the region of 0.22 to 0.50 microns decreased about 30 percent when exposed for about 30 hours. This shows that low-energy protons have more effect on FEP Teflon.

A comparison of the change in solar absorptance $\Delta\alpha_s$ for aluminized FEP Teflon and Z93 is made in Figure 10. Curve A represents the results of JPL (Ref. 7) and Curves B and C represent those of IITRI (Ref. 3). It appears that the test by IITRI was done on Teflon mirrors obtained from JPL. JPL's work shows that the aluminized FEP Teflon degrades more than Z93, whereas IITRI's work shows that although the initial change in solar absorptance is higher than Z93, it changes little thereafter. If the tests done by these two groups are on the same mirrors, then the considerable difference between these data is difficult to understand.

ATTACHMENT METHODS

The optical solar reflectors or the metallized polymers, after they are made, have to be attached to the spacecraft skin for thermal protection of the vehicle. The different methods of attaching an OSR to the vehicle skin is discussed below. Main emphasis is given to the adhesive bonding, since the OSR in general is first attached to a substrate with double-backed tape or silicone adhesive. No data on the attachment of a metallized polymer to the vehicle skin is available. It is likely that the most effective method for OSR attachment may be used for these also.

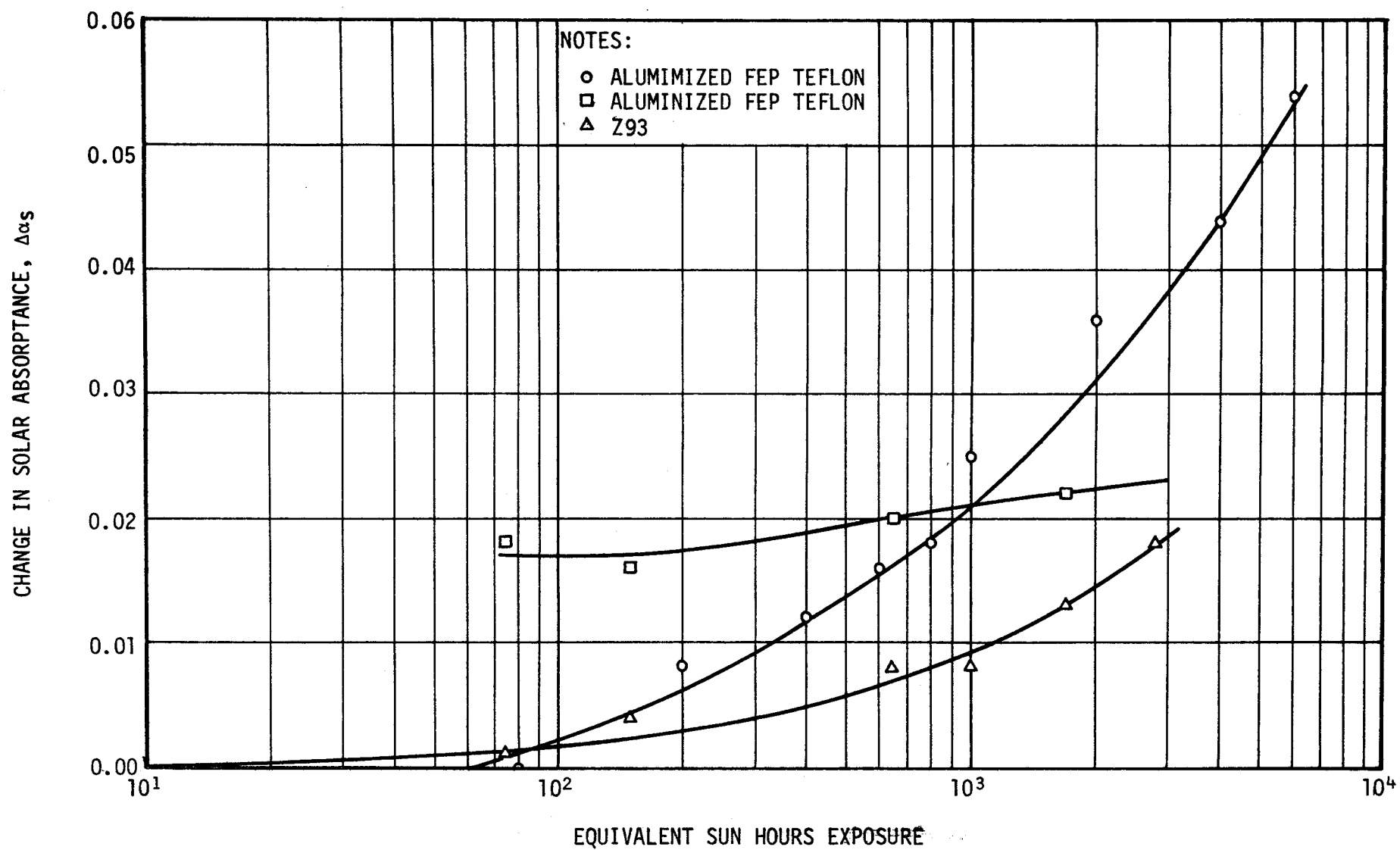


FIGURE 10. DEGRADATION OF ALUMINIZED FEP TEFLON AND Z93

Adhesive Systems

The candidate adhesive materials were: epoxies, polystyrenes, polyesters, and silicones. Of these groups, it was found that the silicone adhesives provided the most desirable characteristics for use with the OSR. According to Lockheed (Ref. 8), of the silicone adhesives tested, General Electric RTV-615 exhibited the most desirable properties.

Ceramic/Silicate Systems - Since the ceramic and silicate systems showed promise in retaining their bonding strength at temperatures in excess of 800°F, LMSC attempted to modify them by adding fillers. It was anticipated that the addition of such materials might reduce the tendency of the silicates to migrate through the protective inconel layer and attack the silver and fused-silica substrate. However, the silvered surface of the second-surface mirrors was degraded whenever brought into contact with the modified silicate/ceramic adhesive systems.

Silicone Systems - The adhesive system which showed the most promising performance characteristics at elevated temperatures and vacuum conditions was a Dow Corning Company silicone under the trade name DC 92-024 Aerospace Sealant, although General Electric RTV-615 was recommended for bonding the OSR to the battery panels for Program 461.

After 14 days of continuous exposure to temperature (800°F) and vacuum (10^{-4} torr) environment, the OSR separated from the substrate. Inspection of the adhesive revealed that all cohesive qualities of the silicone system were destroyed; the material was powdery in appearance. Another specimen which kept for 30 days at temperature and pressure of 710°F and 10^{-4} torr, respectively, was found to be satisfactory.

Visual observation during vacuum-temperature testing of the silicone adhesive showed that the adhesive outgasses heavily at approximately 275°F. Preconditioning at elevated temperature significantly reduced the amount of outgassing, but did not prevent outgassing from occurring at higher temperatures.

Double-Backed Polyimide Tape Systems - The polyimide tape produced by the Permacel Tape Company under the trade name of ST-6962 was also tried. The adhesive system provides a good bond at temperatures below 600°K, but at higher temperatures the tape begins to discolor and the bond line degrades. After 30 days of continuous exposure to temperature (710°F) and vacuum (10^{-4} torr), the mirror separated from the polyimide film. Examination of the specimen revealed that the film was severely charred and very little adhesive remained on either side of the tape.

Epoxy and Phenolic Systems - The epoxy-adhesive system evaluated attacked the silver surface of the mirror and also cracked the mirror. Epoxy and phenolic systems have an inherent lack of elasticity and their resistance to high temperature for prolonged periods is poor.

OSR Attachment to Vehicle Skin

OSRs in the form of 2.54 cm² squares are applied to flat surfaces in a fixture with sliding jig. The radiator surface is coated with a transparent adhesive, and the mirror squares are manually put down as in a tile mosaic. Other means of attaching the mirrors include double-backed tape and mechanical holddowns at edges or corners. Attaching a second-surface mirror to a curved surface is a more difficult proposition. If an adhesive is used, it tends to give at the edges, so that the tiles can pull away, reducing the heat transfer

from the radiator. There have been some cases in which the silver coating separated from the fused silica under simulated launch conditions. Other methods of attachment to the vehicle are described below.

The mirror-substrate assembly was either fixed onto the top layer of a multilayer blanket insulation and the bottom of the multilayer blanket was glued to the vehicle surface; or the mirror-substrate assembly was attached to a substrate mounted to standoffs which pierce through that multilayer blanket and are attached to the vehicle skin by mechanical or adhesive bonding techniques.

Different methods, including thread-and-button, clips, snap-on caps, welding, metallic Velcro fasteners, and adhesives, were tried. Table 1 compares the various methods of fixing the mirror to a substrate and then fixing the assembly to the vehicle.

TABLE 1. ATTACHMENT TECHNIQUES

Elements of Composite System	Attachment Methods	Limitations
OSR TO A SUBSTRATE	<p>Metallic track, clips, tabs</p> <p>Weld to inconel</p> <ol style="list-style-type: none"> 1. Ultrasonic 2. Brazing <p>Adhesive</p> <ol style="list-style-type: none"> 1. Silicones 2. Double-backed tape 3. Ceramic cement 	<p>Subject to thermal warpage</p> <p>Not sufficient film thickness to weld, not replaceable if mirror is shattered during handling</p> <p>Temperature limit 700° to 800°F</p> <p>Temperature limit 500° to 600°F</p> <p>Attack mirror surface. Degrades reflective properties.</p>
MIRROR SUBSTRATE TO MULTILAYER OR TO POST ATTACHED TO VEHICLE	<p>Wires threaded through welded tabs and twisted onto posts</p> <p>Welded snap-on caps fit over posts</p> <p>Mirrors attached to multilayer</p> <ol style="list-style-type: none"> 1. Adhesive or double-backed tape 2. Welded to multilayer <p>Mirror substrate attached to multilayer</p> <ol style="list-style-type: none"> 1. Metallic Velcro fastener 2. Thread into multilayer buttons 	<p>Must have clearance between substrate and multilayer. Bonded posts tend to shear off during handling.</p> <p>Must apply pressure to mirror. Posts and caps are to be made of glass or ceramic to reduce heat loss.</p> <p>Difficult in bonding, no longer removable</p> <p>No technique; available weight causes multilayer to sag.</p> <p>Magnetic material</p> <p>Clearance required, buttons shear off due to load of mirrors</p>
MULTILAYER TO VEHICLE SKIN	<p>Nylon Velcro fastener</p> <p>Metallic clips or snaps</p> <p>Bond bottom</p>	<p>Some alignment necessary for installation</p> <p>Not weldable to aluminized multilayer. Alignment critical</p> <p>Difficulty in bonding system not readily removable or replaceable.</p>

DISCUSSION

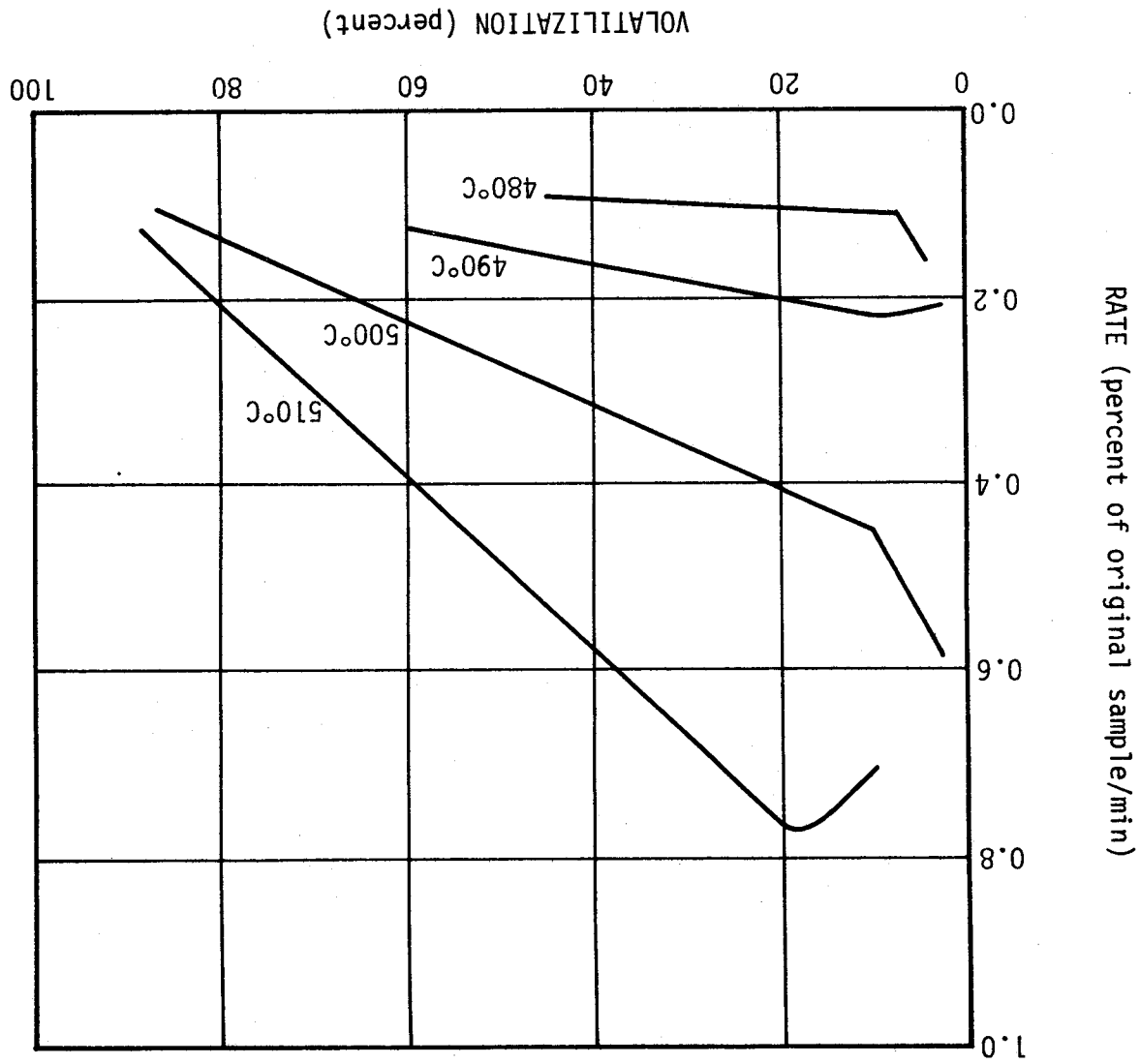
Although OSRs are very stable under irradiation, they have the problem of weight. Moreover, using them on curved surfaces is difficult. If adhesive is used, it tends to give at the edges. All these problems with OSRs are very well-known and hence no further discussion about OSR will be made. Discussions will be confined to the polymers only.

As mentioned before, the metallized polymers are second-surface mirrors, where silver or aluminum is vacuum-deposited on a thin sheet of FEP Teflon, and the Teflon "sees" the Sun and space. It is therefore essential to discuss the effects of temperature and different types of radiations (ultraviolet, proton, electron, and X-rays) on polymers before reaching definite conclusions about the application of metallized polymers for space station thermal control. All the data that are now available on the radiation degradation of FEP Teflon mirrors are on short-duration radiation effects. If these mirrors are to be used for space station thermal control, then the polymer should be thoroughly studied under long irradiation doses. Chain scission in polymers due to thermal, ultraviolet and charged particle radiation has long been recognized (Refs. 9 and 10). In Teflon it is known that once the chain scission is initiated it proceeds rapidly like a chain reaction until the entire chain is consumed.

THERMAL DEGRADATION

A study (Ref. 11) of TFE Teflon from the point of view of thermal stability, composition of degradation products, and rates and activation energy of its depolymerization was made. The results of these measurements are shown in Figures 11 and 12. The rate of

FIGURE 11. RATE OF THERMAL DEGRADATION OF TEFLON AS A FUNCTION OF PERCENTAGE VOLATILIZATION



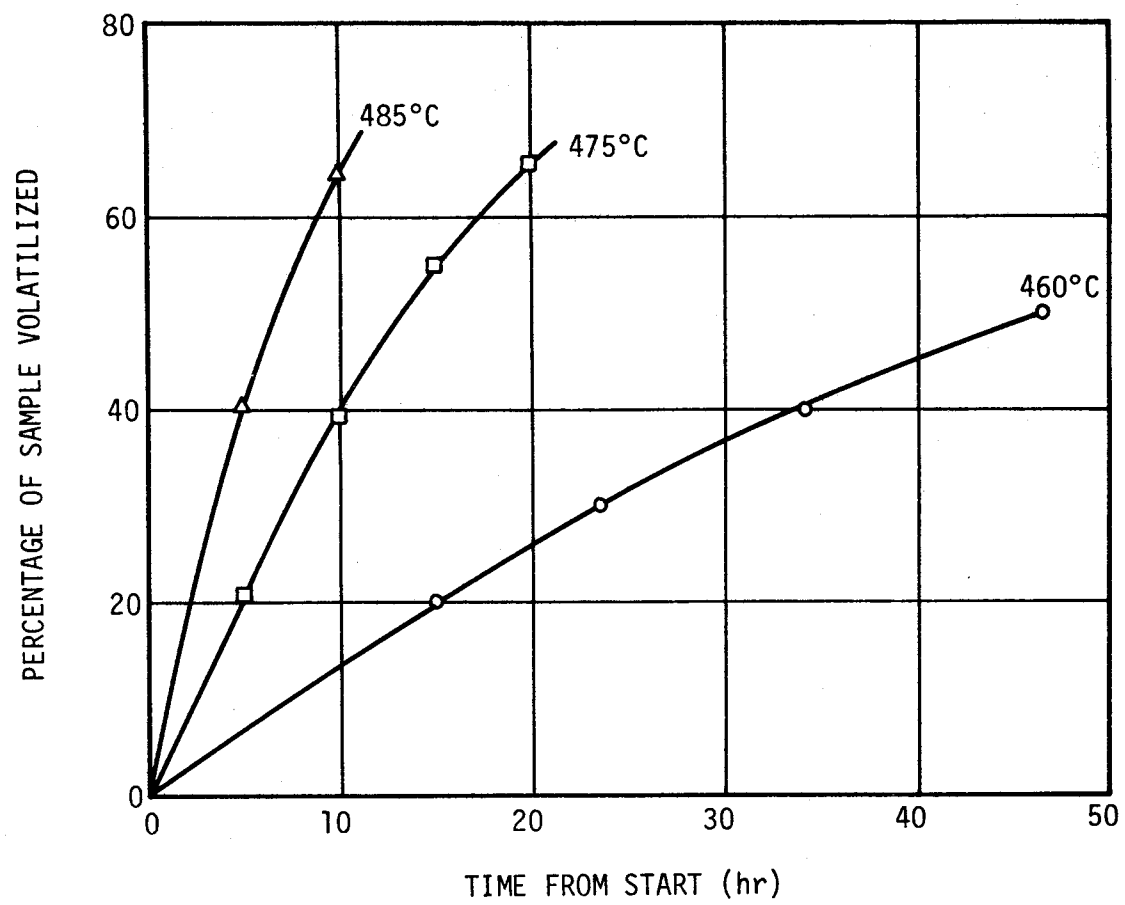
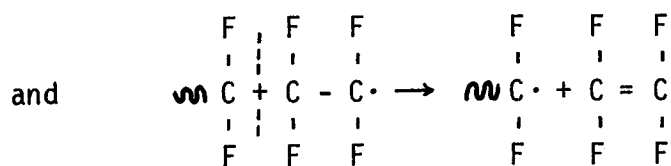
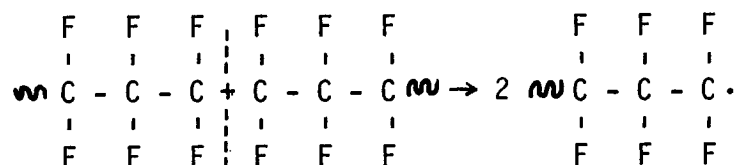


FIGURE 12. CUMULATIVE VOLATILIZATION OF TEFLON AS A FUNCTION OF TIME

thermal degradation (Figure 11) is linear beyond the initial 10 to 18 percent volatilization and point to 100 percent loss at zero rate. This is particularly true at 500 and 510°C pyrolysis. Since TFE Teflon degrades by a first-order reaction, a plot of the logarithm of percent residue as a function of time should result in a straight line, the slope of which is the rate constant, as shown in Figure 13.

The fact that Teflon yields on pyrolysis almost 100 percent monomer suggests a mechanism involving initiation of free radicals which proceed to unzip (chain reaction) rapidly into monomers until the entire chain is consumed. Teflon represents that extreme of the polymer where there is no hydrogen at all on the chain. The F-C bond (107 kcal) is much stronger than the C-C bond (58.6 kcal), so that when a scission of the chain occurs there is no transfer of a fluorine atom. The scission thus results in two free-radical ends which unzip to yield monomers:



When pyrolyzed in a vacuum, or nitrogen, Teflon retains its original shape. In the presence of gases other than nitrogen, the polymer in most cases becomes fluid. Whereas in a vacuum the pyrolyzate from Teflon consists almost exclusively of the monomer, the pyrolyzate from pyrolysis under O₂, H₂ and toluene are altogether different in composition.

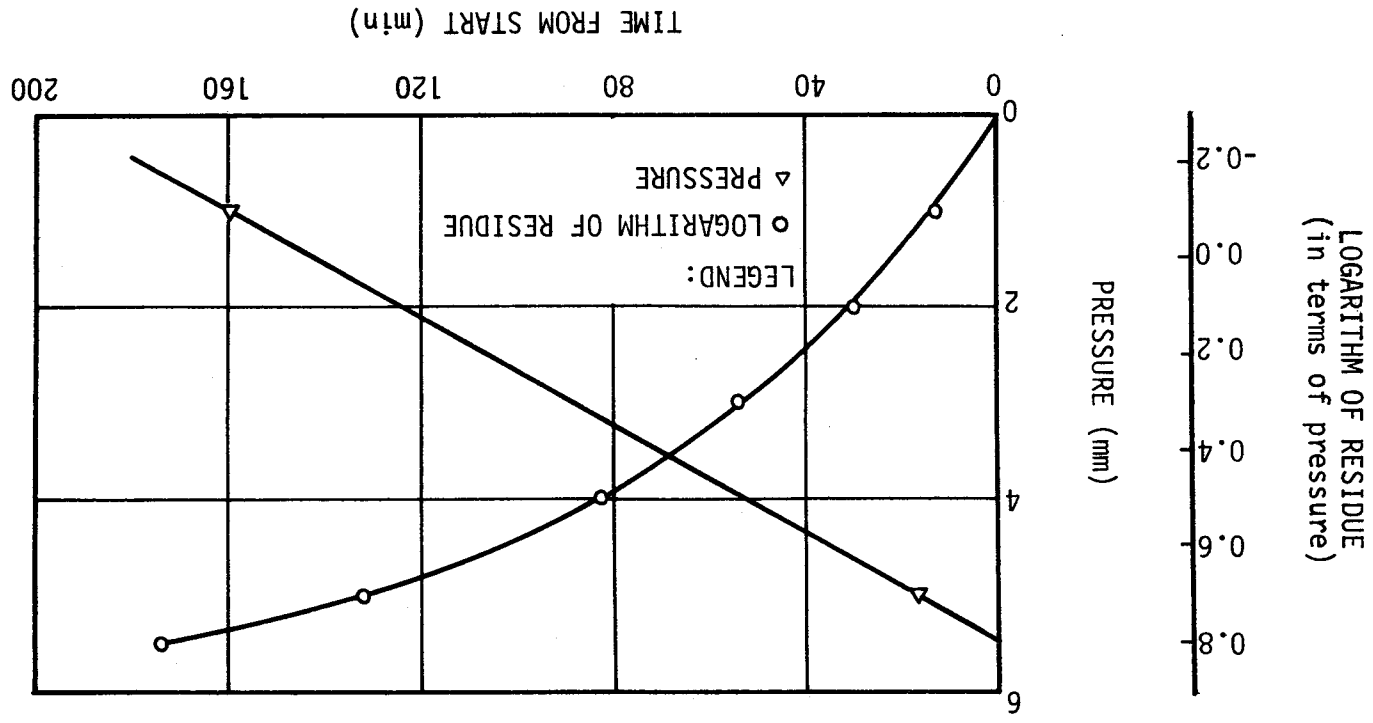


FIGURE 13. RATES OF THERMAL DEGRADATION OF TEFLON AT 513°C

TABLE 2. RELATIVE THERMAL STABILITY OF SOME POLYMERS
(Based on Temperature of Half-life, T_h)

Polymer	Temperature of Half-Life, T_h (°C)	Structure
Kel-F	380	$[-CF_2-CFCl-]_n$
Polymethylene	415	$[-CH_2-CH_2-]_n$
TFE Teflon	509	$[-CF_2-CF_2-]_n$

TABLE 3. ACTIVATION ENERGIES OF THERMAL DEGRADATION OF SOME POLYMERS IN VACUUM

Polymer	Molecular Weight	Temperature Range (°C)	Activation Energy (kcal/mole)
Kel-F	100,000	331.8 - 371	57
Polyethylene	20,000	360 - 392	63
Polymethylene	High	345 - 396	72
TFE Teflon	---	423.5 - 513	80.5

The effect of temperature on the tensile yield strength of Kel-F, FEP Teflon, and TFE Teflon fluorocarbons are shown in Figure 14. Within 11 percent range of crystallinity, there were few differences in properties exhibited at any of the temperatures. One exception of this general agreement was the apparent effect of crystallinity on the tensile modulus of FEP Teflon at cryogenic temperatures. The more crystalline material had low tensile modulus values, especially at the lower temperatures.

IRRADIATION EFFECTS

Burr and Garrison (Ref. 12) found that TFE Teflon loses mechanical strength on exposure to β - and γ -radiation. It evolves other products in addition to CF_4 on irradiation.

Lawton, et al (Ref. 13) placed both TFE Teflon and Kel-F in the class of those undergoing predominant degradation, with no evidence of crosslinking.

Schneider (Ref. 14) has observed that the ESR spectrum of Teflon exposed to X-rays exhibits a symmetrical triplet not observed in the unirradiated polymer. Ard, Shields and Grordy (Ref. 15) found eight equally spaced peaks rather than triplet. When the irradiated polymer was exposed to oxygen, the spectrum rapidly changed and only two bands remained. These findings appear to indicate that actual scission of the polymer chain occurs and that the resulting polymer free radicals remain stable for a considerable time, possibly because in this highly crystalline polymer the severed ends may retract, making recombination impossible.

FEP Teflon, like TFE Teflon, degrades when exposed to high energy radiation, with a resultant adverse effect upon the physical properties. At elevated temperatures it can be crosslinked by use of

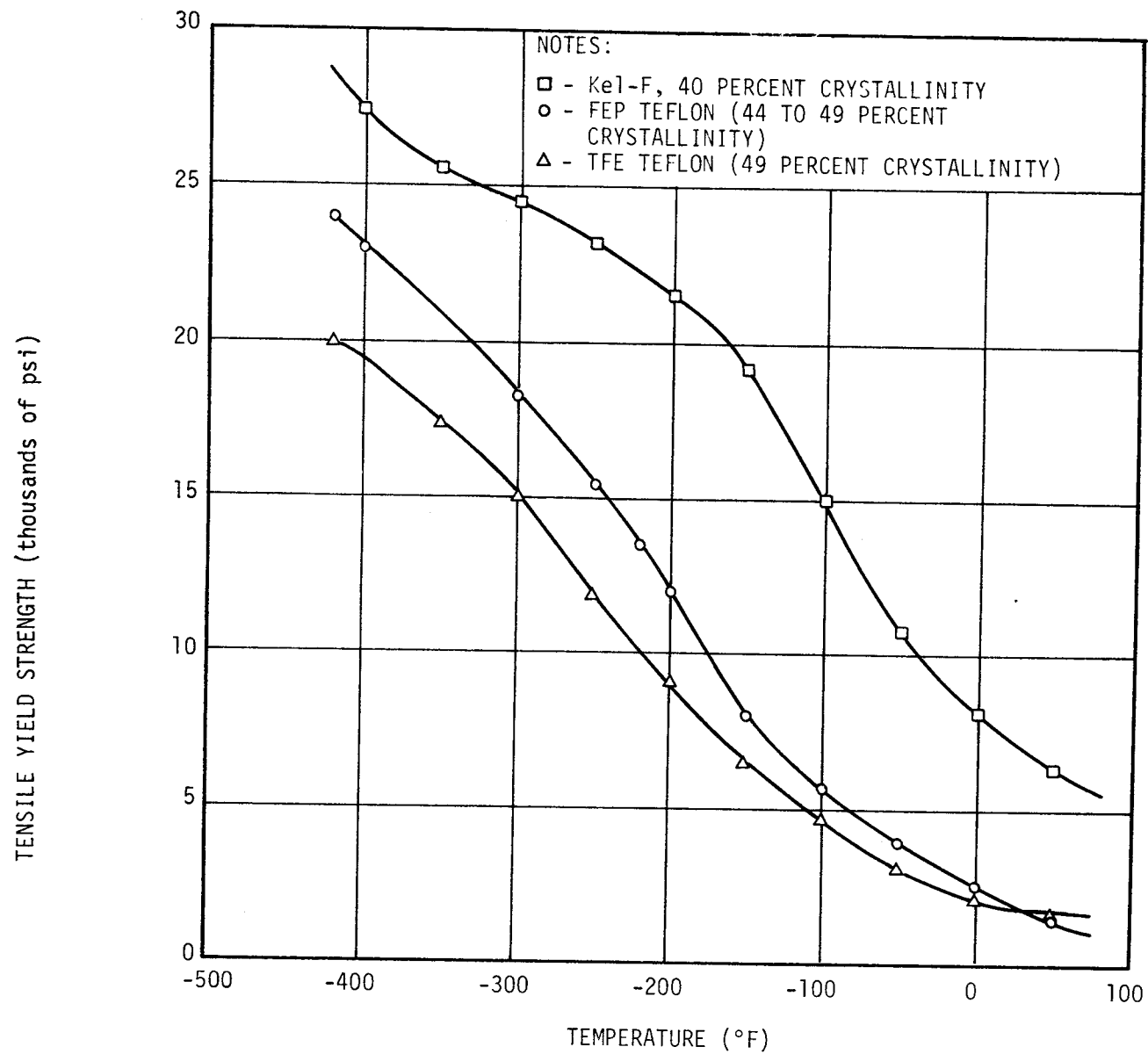


FIGURE 14. EFFECT OF TEMPERATURE ON THE TENSILE YIELD STRENGTH OF FLUOROCARBON PLASTICS

ionizing and ultraviolet radiation. With the introduction of crosslinking reactions, two types of resin became available. One, in which a small amount of crosslinking is introduced, is a resin of altered melt-processing characteristics due to a changed distribution of molecular weights. The other type is crosslinked to the extent that it is incapable of melt processing and, in general, has the high temperature properties associated with a three-dimensional network.

When FEP Teflon is irradiated at room temperature, net degradation results. The decrease in the melt viscosity of the resin due to irradiation in nitrogen atmosphere is shown in Figure 15. If the temperature of the polymer is raised before irradiation, crosslinking predominates, as shown by an increase in melt viscosity. Crosslinking overcomes degradation above 80°C, and at a constant dose of radiation the melt viscosity increases with temperature up through the crystalline melting point. At temperatures greater than 300°C thermal degradation becomes a factor and net increases in viscosity are smaller.

Samples of FEP Teflon given high doses of radiation (100 Mrads) at elevated temperatures in the presence of air become embrittled, while specimens irradiated under nitrogen do not. Radiation at elevated temperatures does cause some reduction in toughness. Tensile impact resistance, flex life, and tear resistance decrease with increased dose. When FEP Teflon is exposed to 1 Mrad of X-rays at elevated temperatures, an increase in viscosity is observed which is of the order of magnitude obtained with 2 MeV electrons. Ultraviolet irradiation also produces degradation reactions at elevated temperatures, although the exposure time is longer than when electrons are used.

The penetration of 500 keV and 1 MeV electrons in Teflon has been measured. The penetration depth in terms of percent relative

APPARENT MELT VISCOSITY
 $[380^{\circ}\text{C ss} = 1.4 \times 10^5 \text{ dynes/cm}^2] \text{ poises} \times 10^{-4}$

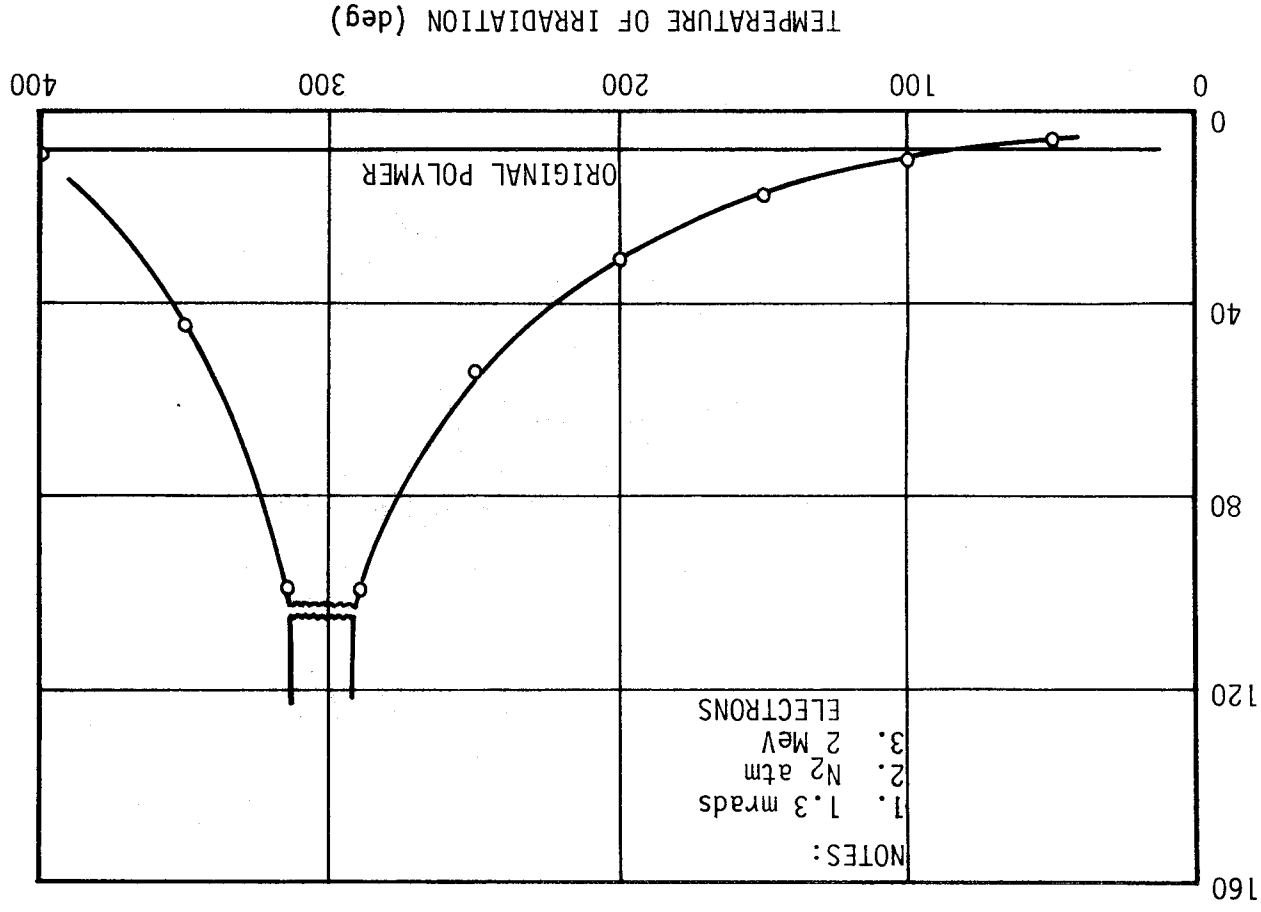


FIGURE 15. EFFECT OF TEMPERATURE OF IRRADIATION ON APPARENT MELT VISCOSITY OF FEP TEFLON

ionization for unit density matter is shown in Figure 16. As is seen, the penetration depth for 500 keV and 1 MeV electron is 20 mils and 67 mils, respectively.

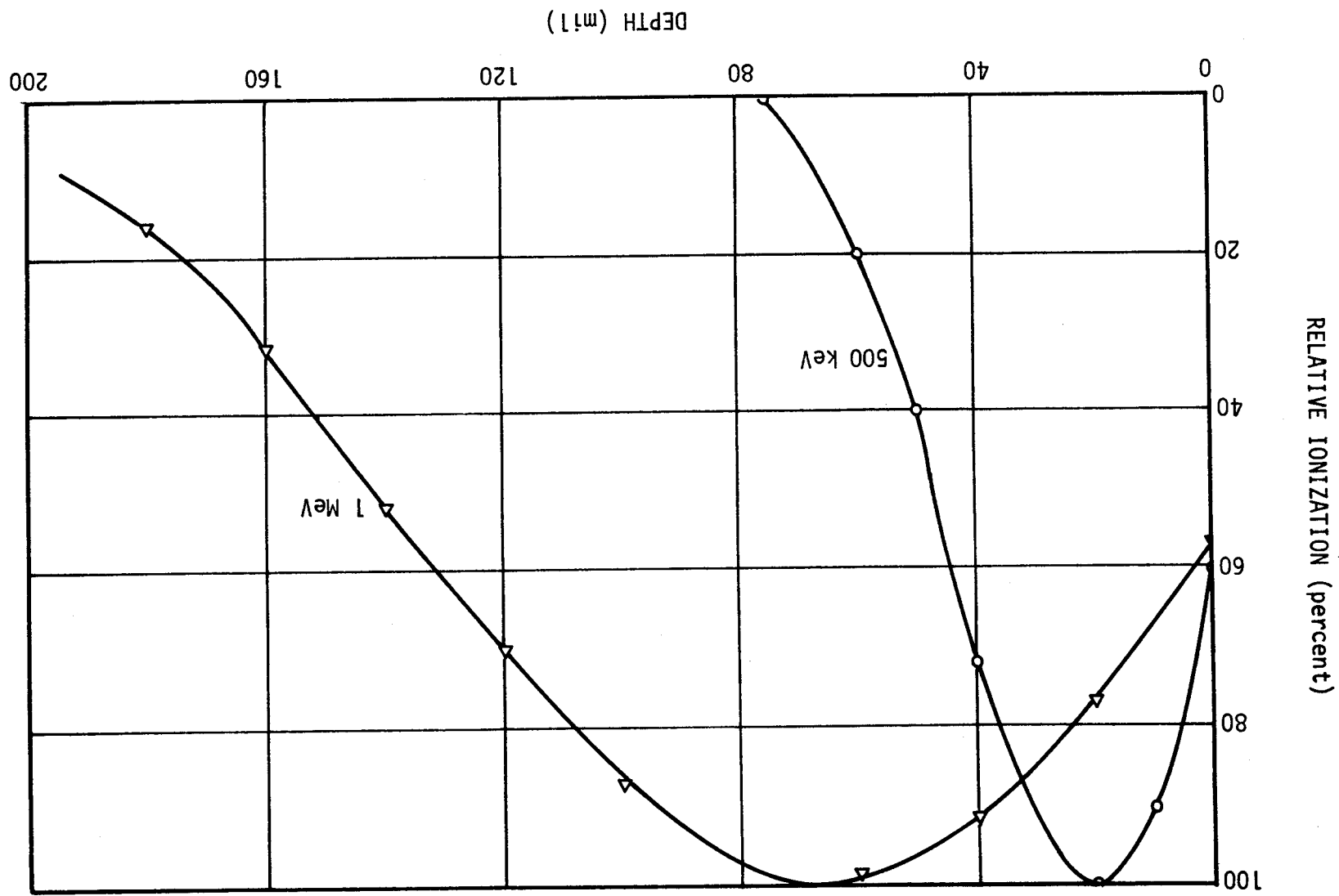


FIGURE 16. PENETRATION OF ELECTRONS IN UNIT DENSITY MATTER (ONE SIDE IRRADIATION)

CONCLUSIONS AND RECOMMENDATIONS

Both the ultraviolet and the soft X-ray component of the solar spectrum possess sufficient energy per quantum to induce rupture of many chemical bonds and thus initiate chemical reactions.

Organic polymers, because of the dependence of their bulk physical properties on molecular weight and the integrity of their skeleton which is made up of carbon to carbon bonds or other covalent linkages, are more susceptible to degradation than metals, ceramics, and inorganic compounds which are held together primarily by the stronger coulombic interactions between atoms.

These organic or polymer materials are subject to a wide range of radiation effects in varying degrees depending on their structure. Damage to such compounds is a function of the energy absorbed from the radiation source, regardless of its type. In most cases the energy is stored in the electrons of the individual molecule, thereby raising them to an excited state. The result of this unstable energy condition is 1) either the electron is raised to a high-energy level but remains bound to the parent nucleus or 2) the electron is removed from its parent nucleus, giving rise to a free electron. This gives rise to broken bonds and if unpaired electron results, the product is a free radical. The other most common products are ions. The recombination of radicals and ions in organic compounds results in crosslinking, chain scission, chain polymerization, block copolymerization, unsaturation, and chain transfer. These reactions may result in gradually changing the rigidity of an elastomeric material until a glasslike substance results. In the chain scission or cleavage, long polymer chains are broken up into fragments with subsequent drastic changes in physical and mechanical properties.

Optical changes also occur in organic materials. Most transparent polymers darken with radiation. Radiation reduces the size of large crystallites in polyethylene, while at the same time increasing the number of smaller ones and resulting in a change of transparency.

There are several possible explanations for a dose-rate effect of polymer degradation. On a molecular scale, the initial breakdown of polymer chains could be independent of dose-rate, but then be followed by a time-dependent process leading to physical breakdown. Such a process might be the diffusion of radiation into the polymer. It has been suggested that even if the immediate effect of radiation is a time-independent chain breakage, the deterioration in mechanical properties might result from a time-dependent development of cracks and fissures (Ref. 16).

Exposure of FEP Teflon to solar ultraviolet, electron, and proton radiations can give rise to degradation, manifested by cracking, discoloration, and polymer chain scission. However, cracking can result in increased permeability to gases. Discoloration may lead to the attainment of higher equilibrium temperatures in space due to an increase in solar absorptivity of the surface. Polymer chain scission process can lead to complete depolymerization and softening, thereby completely destroying the thermal control property.

The penetration of electrons into Teflon has already been discussed. The thickness of Teflon used for the mirrors is generally between 1 to 5 mils. Hence it may be possible for electrons and protons to penetrate this thickness and reach the boundary between the polymer and silver or aluminum. This phenomena may cause a break in the bonding between the metal film and the polymer and produce "bubbling". Such an effect has been observed (Ref. 6). This will affect the α_s to ϵ ratio and drastically change the thermal control property of the metallized polymer.

The evaporation of the volatile components formed due to the thermal degradation of the polymer in space can result in deposition of the outgassed products on optical surfaces and contaminate them. Such deposition can produce marked changes in optical properties, including spectral absorptance, reflectance, and transmittance which can be detrimental to the performance of the optical component.

These problems may be more severe for long-term missions such as Skylab and space stations using metallized polymers as thermal control coating. To overcome these difficulties, each design must be optimum, and to do this effectively, a better understanding of the properties of the polymers and their interaction with the space environment must be reached.

REFERENCES

1. Marshall, K. N. and R. A. Breuch, J. Spacecraft, 5, 1051 (1968)
2. Gillette, R. B., J. Spacecraft, 5, 454 (1968)
3. Zerlaum, G. A., et al, "Study of In Situ Degradation of Thermal Control Surfaces", IITRI Report U6061-17, NASA Contract NAS8-21074, March 1969
4. Heaney, J. B., "Results from ATS-3 Reflectometer Experiment", NASA Goddard Space Flight Center,
5. Fogdall, L. B., et al, "Electron Energy Dependence for In-Vacuum Degradation and Recovery in Thermal Control Surfaces", NASA Contract NAS5-11164, Presented in AIAA 4th Thermophysics Conference,
6. Wilks, D. R., Marshall Space Flight Center, Huntsville, Alabama, Private Communication
7. Carroll, W. F., "Stable Temperature Control Surfaces for Spacecraft", JPL Report 32-340, NASA Contract NAS7-100, November 1962
8. Marshall, K. N. and R. L. Olson, "Optical Solar Reflector Thermal Control Surface", Lockheed Report LMSC 3-56-65-2, February 1965
9. Madorsky, S. L., Thermal Degradation of Organic Polymers, Interscience Pub., 1964
10. Bovey, F. A., The Effects of Ionizing Radiation on Natural and Synthetic High Polymers, Interscience Pub., 1958
11. Madorsky, S. L. and S. Straus, J. Research Natl. Bur. Stand., 64A, 513 (1960); 66A, 401 (1962)
12. Burr, J. G., and W. M. Garrison, U. S. Atomic Energy Commission Report AECD-2078 (1950)
13. Lawton, E. J., A. M. Beuche, and J. S. Balwitt, Nature, 172, 76 (1953)
14. Schneider, E. E., J. Chem. Phys. 23, 978 (1955)

15. Ard, W. B., H. Shields, and W. Gordy, J. Chem. Phys.,
23, 1727 (1955)
16. Charlesby, A., Atomic Radiation and Polymers, Pergamon
Press, 1960